Process development for hydrometallurgical recovery of valuable metals from sulfide-rich residue generated in a secondary lead smelter

Eunyoung Kim, Joris Roosen, Liesbeth Horckmans, Jeroen Spooren, Kris Broos, Koen Binnemans, Karl C. Vrancke, Mieke Quaghebeur

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ABSTRACT

Two routes were investigated to selectively recover lead and minor metals (Cu, Ni, Zn) from a sulfide-rich lead smelting residue, matte. The first route comprises a two-step leaching process that combines Fe(III)-HNO₃ leaching with roasting, followed by water leaching. In the first step, the efficiency of Pb leaching was 90% at the optimum condition (L/S ratio 8, 0.5 mol·L⁻¹ HNO₃, 0.15 mol·L⁻¹ Fe(III), 25 °C). In the second step, roasting at 600 °C followed by water leaching at 50 °C selectively leached Ni, Cu, and Zn while fully converting iron sulfides to oxides. One-step oxidative pressure leaching in HNO₃ was investigated as an alternative to simultaneously leach Pb, Cu, Ni and Zn. At the optimal conditions (130 °C, 60 min, 0.3 mol·L⁻¹ HNO₃, 0.07 mol·L⁻¹ Fe(III), L/S ratio 20), Pb, Cu, Zn and Ni leaching were 92, 60, 70 and 66%, respectively, while Fe leaching remained low (2%). The leachates obtained from both leaching routes were treated by ion-exchange adsorption with diethylenetriaminepentaacetic acid (DTPA) functionalized chitosan-silica hybrid materials to investigate the selective recovery of Cu, Zn and Ni. The adsorption order appeared to be in the same order as the corresponding stability constants for complexes between the respective metal ions and free DTPA: Ca(II) < Zn(II) < Pb(II) = Ni(II) < Cu(II). This allows not only to selectively recover Cu, Zn and Ni from the leachates, but also to mutually separate them by using the functionalized resin as a stationary phase in column chromatography. To avoid adsorbent contamination, Fe(III) and Pb(II) may be removed from the leachates in a pre-treatment step. Based on these results, the investigated methods can be combined as process steps of two possible routes for the selective recovery of valuable metals from the studied secondary lead smelting residue. The two-step leaching process seems to be superior since a more concentrated solution of Cu, Ni, and Zn is produced in the 2nd leaching step with low capital cost.

1. Introduction

It is estimated that each year worldwide over 500 million rechargeable lead acid batteries are produced (Vasant et al., 2013). In Europe and the US, the recycling rate from spent batteries is higher than 98% (EUROBAT). The recovery of metallic lead from spent batteries usually takes place by pyrometallurgical processes. For each ton of metallic lead produced, 100–350 kg of slag is generated that contains approximately 5% of lead compounds and hazardous minor elements such as copper, tin, antimony, nickel, and zinc (Shu et al., 2015).

Galena (PbS) is the main lead compound contained in the Pb slag. In order to recover Pb, leaching of the natural mineral galena has been investigated by many researchers who proposed different HNO₃-based leaching systems, including HNO₃ (Zárate et al., 2012), H₂O₂-HNO₃ (Aydoğan et al., 2007a) and Fe(III)-HNO₃ (Pashkov et al., 2002). Also, chloride systems can leach galena but require high brine concentrations and elevated temperatures to promote the formation of soluble chloride complexes to increase the solubility of lead chloride, i.e. (NaCl-)HCl (Zhang et al., 2015) or FeCl₃-HCl/H₂O₂-HCl (Baba and Adekola, 2011). As an alternative, fluorosilicate as a lixiviant (Habashi, 2005) or acetic acid leaching in the presence of hydrogen peroxide (Aydoğan et al., 2007b) was reported. Meanwhile, processing of lead batteries has often been taken up by treating the PbSO₄ sludge separately, for which a number of processing methods mostly based on leaching with NaOH (Liu et al., 2012) or citric acid (Zárate and Lapidus, 2014) and electro-winning/precipitation have been developed (Agrawal et al., 2004). There are few studies aimed at leaching or recovery of lead from secondary lead smelting slags (Ettler et al., 2004; Smaniotto et al., 2007b).
Nitrate-based hydrometallurgical processes have some unique and advantageous characteristics. Nitric acid can produce highly oxidizing conditions and is an effective leachant for most sulfides (Shang and Weert, 1993; Gok and Anderson, 2013). Another important advantage of the nitrate system over the sulfate and chloride ones is that NO₃⁻ reacts readily with oxygen to regenerate nitric acid at high temperature (> 120 °C) (Gok and Anderson, 2013). Furthermore, the reaction rates of the nitrate system over the sulfate and chloride ones is that NO(g)


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One of these effective technologies is ion-exchange adsorption. Ion-exchange adsorption is considered as a key technology to recover low concentrations of valuable metals from large volumes of waste water (Igwe, 2007; Roosen et al., 2014). A wide variety of ion-exchange resins, able to sequester metal ions from aqueous solutions, are commercially available and industrially applied, such as Duolite®, Dowex®, and Amberlite® (Pennington and Williams, 1959; Eldridge, 2000). However, these materials suffer from low loading capacities, often show high swelling behavior and they are very expensive (Miller et al., 1981). The high availability of low-cost biosorbents make them interesting alternatives for metal recovery, provided that modifications of the material's structure is straightforward. Chitosan is a linear polysaccharide derived from seafood waste (shrimps, lobsters, crabs) and its adsorption behavior has been widely studied in the context of water purification and metal recovery (Gerente et al., 2007; Guibal, 2004; Wang and Chen, 2009). The abundant availability of amino and hydroxyl groups enables chemical modification of this biopolymer. This way, its adsorption performance, such as the selectivity, can be easily adjusted (Zhao et al., 2013; Roosen and Binnemans, 2014). In analogy with EDTA-modified chitosan-silica, first described by Repo et al. (2011), DTPA-functionalized chitosan-silica hybrid materials can be synthesized and their adsorption performance for Cu, Zn and Ni from leachate solutions investigated. Hybridization with silica improves the mechanical properties, the chemical resistance and the porosity (Liu et al., 2010). By these chemical and physical modifications, functionalized chitosan-silica hybrid materials are expected to become suitable for use as the stationary phase in chromatography columns, on a larger scale than laboratory scale.

In this study, we aimed to selectively recover Pb, Cu, Zn and Ni from a secondary lead smelting residue by investigating and optimizing their leaching behavior in nitric acid by means of a two-stage and a one-step leaching process. Furthermore, separation of Cu, Zn and Ni from the leachates was tested for the first time by ion-exchange adsorption chromatography with DTPA-functionalized chitosan-silica hybrid materials. Finally, it was aimed to valorize the iron-rich matrix material after leaching in view of total recycling of the waste material (near zero-waste valorization).

### Table 1

<table>
<thead>
<tr>
<th>Elements</th>
<th>Fe</th>
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<th>Cu</th>
<th>Ni</th>
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### 2. Materials and methods

#### 2.1. Materials

The lead smelting residue was collected at a lead smelting company. The residue was produced in a shaft furnace fired with coke and loaded with a charge composed of lead scrap, iron scrap (flux), and lime (additive). The smelted and molten residue which consists of two layers, i.e., matte (sulfur-rich layer, more dense) and slag (oxides), were tapped off into a cone-shaped pot, cooled, turned over and physically separated. The > 15 cm size fraction of the slag phase is reused in the process and the remainder of the slag and matte are currently disposed. In this study, the disposed matte was used as sample. The matte sample was taken according to the Flemish standard CMA/1/A.15 (CMA/1/A.15, 2012). Representative samples for the leaching tests were obtained after crushing and sieving to a particle size below 125 μm. The chemical (Table 1) and mineralogical composition (Fig. 1) of the matte sample was determined. The matte mainly consists of iron (50%) as FeS (trolite) and FeO (wüstite), and lead (about 7%) as PbS (galena) and metallic lead phases. Also, it contains minor amounts of PbO (litharge), Fe₂SiO₄ (fayalite) and Fe₃O₄ (magnetite).

#### 2.2. Leaching

##### 2.2.1. Roasting

Roasting of the matte sample (< 125 μm) was carried out in an alumina crucible, which was placed in a temperature controlled muffle furnace. The sample was heated at a rate of 2 °C·min⁻¹ to a set temperature between 400 °C to 700 °C and held for 2 h at this temperature. Mass change during the reaction was measured by weighing the sample before and after roasting. Subsequently, the roasted matte sample was leached with water.

##### 2.2.2. Atmospheric leaching

The atmospheric leaching tests were carried out in a 60 ml polytetrafluoroethylene (PTFE) bottle with cap on 2.0 g of the un-roasted or the roasted matte samples with a particle size smaller than 125 μm. A typical experimental procedure consisted of mixing the sample with a predetermined liquid-to-solid mass ratio of reagent in the

![Fig. 1. XRD patterns of the matte used in this study.](image-url)
2.2.3. Autoclave leaching

Leaching tests were carried out in a 100 mL PTFE-lined, stainless steel autoclave system (Parr, model 4842), equipped with a digital temperature control unit to steer the heating power of the external heating mantle. The reactor was charged with 40 mL of a solution with a predetermined HNO₃ concentration and 2.0 g of matte sample (< 125 μm) in the presence or absence of Fe(NO₃)₃. Next, the reactor was heated to the desired temperature (130 to 180 °C) with an autogenous pressure built up of 5.8 to 36 bar total pressure with building up the auto-pressure. The temperature inside the reactor was measured with a thermocouple, connected to a digital multi-meter. At the end of the reaction, the heating system was switched off and the reactor was allowed to cool down to room temperature in the surrounding air. The oxidation-reduction potential (ORP) was measured at room temperature after opening the reactor.

2.2.4. Analytical methods

After each leaching experiment, the slurry was filtered by filter paper (Whatman) of 0.45 μm pore size and the obtained filtrate was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Elemental) to determine the amount of metal extraction. Furthermore, ORP (mV[Aq/H⁺]) of the solution was measured by a SenTIX ORP 900 electrode. The obtained solid residues and original sample before leaching were analyzed by X-ray fluorescence (XRF, Thermo Scientific) and X-ray diffraction (XRD, Philips) in order to determine the chemical and mineralogical composition, respectively.

2.3. Ion-exchange (IX) adsorption from leachate

2.3.1. Synthesis sorbent material

Both batch and column adsorption experiments were performed with diethylenetriaminepentaacetic acid (DTPA) functionalized chitosan-silica hybrid particles. The synthesis of DTPA-chitosan-silica is described in detail elsewhere (Roosen et al., 2014). Shortly, chitosan and tetraethyl orthosilicate (TEOS) are combined to obtain a more stable chitosan-silica hybrid material through hydrolysis and subsequent silica condensation reactions. The latter material is then reacted with diethylenetriaminepentaacetic acid (DTPA) functionalized chitosan-silica polymer matrix, through formation of amide bonds with the bisanhydride of DTPA to immobilize the organic ligand on the silica matrix. The synthesis of DTPA-chitosan-silica is optimized in a previous study (Kim et al., 2017). The optimum pH for Pb leaching was 25 °C. As the temperature increased, Pb leaching was decreased due to PbSO₄ precipitation, while the leaching efficiencies of Ni, Cu, and Zn in the tested leaching system were not significant. The effect of acid concentration and additional oxidant on metal leaching at 25 °C is presented in Fig. 2. The Pb leaching increased from 63% to 69% upon increasing HNO₃ concentration from 0.2 mol·L⁻¹ to 0.5 mol·L⁻¹. Furthermore, when 0.15 mol·L⁻¹ Fe(III) as Fe(NO₃)₃ in 0.5 mol·L⁻¹ HNO₃ was added as an additional oxidant the Pb leaching was enhanced to 89% (Fig. 2). Besides, the leaching efficiency of other metals (Ni, Cu, and Zn) was around 20 to 30%.

2.3.2. Batch adsorption

Preliminary adsorption experiments were conducted in batch mode. Functionalized particles were weighed and added to the vials, containing synthetic metal solution or leachate solution (10 mL). The experimental pH was varied by addition of 1.0 mol·L⁻¹ HNO₃ to decrease, or 0.1 mol·L⁻¹ NaOH to increase the pH, respectively. Solutions were stirred at room temperature with a magnetic stirring bar at 500 rpm for 4 h. Next, the particles were separated from the aqueous solution by filtration, making use of a regenerated cellulose syringe filter with a pore size of 0.45 μm. The remaining metal-ion concentration of the aqueous solution was measured using total-reflection X-ray fluorescence (TXRF, vide infra). The adsorption efficiency for each metal ion is expressed as the recovery percentage:

\[
\% \text{recovery} = \left( \frac{c_i - c_f}{c_i} \right) \times 100\%
\]

(1)

In this expression, \(c_i\) is the initial metal ion concentration in aqueous solution (mmol·L⁻¹) and \(c_f\) is the equilibrium metal ion concentration in aqueous solution (mmol·L⁻¹).

2.3.3. Column separation

The column chromatography setup was composed of a Büchi chromatography pump B-688, to control the pressure and the eluent flow, and a glass Büchi BOROSILIKAT 3.3 column tube N 17988, with dimensions 9.6 mm × 115 mm (bed volume = 8.3 mL). To pack the columns, DTPA-chitosan-silica (2.0 g) was soaked in an aqueous HNO₃ solution. Then the stationary phase was poured in the column. Pressurized air was used to ultimately pack the wet resin slurry. Metal filter frits were mounted at the top and at the bottom of the column. The pressure maximum was set at 10 bar. Separated compounds were collected with the aid of a Büchi Automatic Fraction Collector B-684. Each experiment was preceded by thorough washing of the column with deionized water (50.0 mL), followed by conditioning of the column with an aqueous HNO₃ solution (50.0 mL), set at a certain pH (pH = 5.00 in the first column experiment and pH = 2.00 in the second column experiment). Then the leachate sample (5.0 mL) was loaded and elution was initiated. The flow rate was set at 1 mL·min⁻¹. Different column fractions (5.0 mL) were collected in conical tubes. A decreasing pH gradient was applied during elution by increasing the HNO₃ concentration of the eluent solution. Final stripping of the column was done with a 1.0 mol·L⁻¹ solution of HNO₃. The distinct fractions were monitored by ex-situ analysis of the fractions with TXRF.

2.3.4. Analytical methods

Metal-ion concentrations were determined by means of TXRF on a Bruker S2 Picoflex TXRF spectrometer. The sample preparation for a TXRF measurement consists of mixing the unknown metal ion solution (100 μL) with a 1000 mg·L⁻¹ Ga standard solution (100 μL) and water (800 μL) in an Eppendorf tube. A certain amount of this prepared solution (5 μL) is put on a small quartz plate, pre-coated with a hydrophobic silicone solution (10 μL), and dried in an oven at 60 °C.

3. Results and discussion

3.1. Atmospheric leaching

3.1.1. Fe(III)-HNO₃ leaching

As a preliminary test, the boundary conditions with regard to nitric acid and additional oxidants (i.e. ferric ion) concentrations on Pb and Fe leaching from the matte phase were thoroughly investigated and optimized in a previous study (Kim et al., 2017). The optimum temperature for Pb leaching was 25 °C. As the temperature increased, Pb leaching was decreased due to PbSO₄ precipitation, while the leaching efficiencies of Ni, Cu, and Zn in the tested leaching system were not significant. The effect of acid concentration and additional oxidant on metal leaching at 25 °C is presented in Fig. 2. The Pb leaching increased from 63% to 69% upon increasing HNO₃ concentration from 0.2 mol·L⁻¹ to 0.5 mol·L⁻¹. Furthermore, when 0.15 mol·L⁻¹ Fe(III) as Fe(NO₃)₃ in 0.5 mol·L⁻¹ HNO₃ was added as an additional oxidant the Pb leaching was enhanced to 89% (Fig. 2). Besides, the leaching efficiency of other metals (Ni, Cu, and Zn) was around 20 to 30%.

3.1.2. Roasting followed by water leaching

Oxidation of FeS is necessary to decrease the dissolution of iron and transform the minor valuable metal (Ni, Cu, Zn) sulfides into oxidic metal compounds that are easily soluble in water or weak acid. In the second step oxidation is achieved by roasting with subsequent water leaching to recover Cu, Ni, Zn while keeping Fe in the residue.

3.1.2.1. Roasting. In order to determine the roasting boundary conditions, matte sample was roasted at different temperatures between 400 and 700 °C. Fig. 3 shows the XRD results of the matte sample treated at different roasting temperatures. As shown in the figure, the FeS reflections disappeared at 500 °C and reflections of Fe₂O₃ appeared, after which the intensities of the Fe₂O₃ reflections
increased with increasing temperature indicating the formation of a more crystalline phase. The thermal analysis of FeS under oxidative conditions was reported by Kennedy and Sturman (1975). This work also supports that FeS was dominantly converted to FeSO₄ with accompanying formation of Fe₃O₄, Fe₂O₃ and FeS₂ within the temperature range between 425 and 520 °C, causing a mass increase. Oxidation to Fe₂O₃ is complete at 725 °C. However, the PbS and Pb phases were transformed into insoluble PbSO₄ above 400 °C, inferring that Pb phases should be leached before the roasting step.

### 3.1.2.2 Water leaching after roasting

As presented in Fig. 4, the leachability of Ni, Cu, and Zn in water (50 °C, L/S 10) after roasting was also strongly affected by roasting temperature. Maximum leaching efficiency was 97% for Cu at 550 °C, 55% for Ni at 650 °C, and 50% for Zn at 600 °C. The decreased leaching efficiency above 650 °C may be due to the conversion to insoluble metal oxides or oxysulfates (Dunn, 1997). Taking into consideration the optimal leaching conditions of the three metals, as well as the minimal leaching of iron, 600 °C is considered the optimal roasting temperature.

Fig. 5 shows the effect of the water leaching temperature after roasting at 600 °C. As shown in the figure, leaching of Cu was almost stable between 76 and 80% indicating that the leachability is not significantly affected by leaching temperature. For Ni and Zn leaching slightly increased from 32 to 44% and from 46 to 54% with increasing temperature from 25 °C to 70 °C, respectively.

### 3.2 Oxidative pressure leaching

Aqueous oxidation methods have attracted increasing attention in view of environmental and economical perspectives (less emission of gas and lower operating temperature with respect to roasting). The aqueous oxidation can be operated at elevated temperatures and pressurized conditions. Furthermore, Fe(NO₃)₃ self-decomposes at elevated temperatures in autoclave systems, yielding hematite and NO(g) with minor NO₂(g). The nitrous gases are regenerated under closed vessel conditions as nitric acid above 120 °C (Shang and Weert, 1993). Compared to atmospheric leaching, the regeneration of HNO₃ in a closed system allows the process to be operated with lower acid concentrations and higher oxidation power. Oxidative pressurized leaching in HNO₃ was investigated as a possible leaching step.

Generally, as temperature increases (> 100 °C) sulfur oxidation is enhanced (Mackiw et al., 1966), transforming sulfide minerals into
sulfate. This results in decreased Pb leaching due to PbSO₄ or lead jarosite precipitation (Zárate et al., 2012). Therefore, it is difficult to simultaneously recover Pb, and other base metals such as Ni, Cu, and Zn from sulfide minerals in nitric acid at elevated temperatures.

Leaching with HNO₃ in varying concentrations was investigated at 130 °C to find the optimal leaching condition to enhance Pb, Cu, Ni, and Zn leaching and avoid Fe dissolution at the same time. An autoclave system was applied to perform tests. As shown in Fig. 6, Zn, Cu, and Ni show increasing leaching efficiency with increasing HNO₃ concentration from 0.1 up to 0.75 mol⋅L⁻¹. However, Pb leaching was maximum (84%) at 0.3 mol⋅L⁻¹ HNO₃ then decreased with increasing ORP (oxidation power) to 83% at 0.5 mol⋅L⁻¹ and 55% at 0.75 mol⋅L⁻¹. To enhance Pb leaching, 0.3 mol⋅L⁻¹ HNO₃ was chosen for further study.

The effect of Fe(III) ion concentration at 130 °C is presented in Fig. 7. Lead and copper leaching linearly increased with Fe(III) ion concentration. The maximum Pb and Cu leaching was 92 and 60%, respectively, at the highest Fe(III) concentration of 0.07 mol⋅L⁻¹ Fe(III). Ni (67%) and Zn (71%) leaching was maximum at 0.05 mol⋅L⁻¹ Fe(III) and remained at this level for higher Fe(III) concentrations. It is noteworthy that the iron leaching was below 3% (< 500 mg⋅L⁻¹) and much lower than in atmospheric leaching (Fe 22%). The addition of 0.07 mol⋅L⁻¹ Fe(III) was chosen as the optimum condition.

The leaching temperature is also an important parameter. Leaching of Pb decreases with increasing leaching temperature (Fig. 8), whereas the leaching of Cu, Ni, Zn was increased to 62, 76, 74%, respectively, at 160 °C and then decreased again. The decreased leaching efficiency at 180 °C may be due to the inclusion of Cu, Ni, Zn in the jarosite crystal phase. Therefore, 130 °C was selected as the optimum leaching temperature.

Fig. 9 shows the effect of leaching time. Lead leaching was slightly increased from 88% to 92% by increasing leaching time from 15 to 60 min and then decreased to 52% at 120 min. For Fe, leaching...
3.3. Optimal leaching conditions

20% of sulfur goes into solution (decrease from 20 to 16 wt%). After leaching trends of Cu, Ni and Zn are similar to that of Fe leaching, the decreased with time until a minimum of 0.4% at 120 min. For the other metals, highest leaching efficiency was reached at 30 min (Cu, Zn) or 60 min (Ni) followed by a slight decrease after 120 min. Since the leaching trends of Cu, Ni and Zn are similar to that of Fe leaching, the decrease leaching efficiency of these minor metals may be due to co-precipitation with Fe (e.g. jarosite or oxides). Furthermore, in future scale-up studies, the cooling conditions of the reactor system require a more in-depth study since currently the reactor systems were cooled in air and not quenched. Therefore, the reaction times of the reported experiments might be somewhat longer than reported. For all metals, leaching was drastically decreased when the liquid-to-solid (L/S) ratio was decreased from 20 to 10 (Fig. 10). With decreasing L/S ratio, the ORP was also drastically decreased indicating the deficiency of oxidants as shown in Fig. 10. Also, the pH was increased from 2.4 to 4.8 with decreasing L/S ratio. Therefore, the decrease of leaching efficiency may be due to the consumption and consequential lack of oxidants and acids.

Based on the above results, the optimal condition of pressure leaching to selectively leach Pb, Ni, Cu, Zn is 130 °C, 60 min, 0.3 mol·L⁻¹ HNO₃, 0.07 mol·L⁻¹ Fe(III), L/S ratio 20.

3.3. Optimal leaching conditions

Two processes were investigated to recover valuable metals from matte. The first process is a two-step approach combining Fe(III)-HNO₃ leaching at 25 °C with roasting at 600 °C, followed by water leaching. The second process is a one-step oxidative pressure leaching in nitric acid (autoclave, 130 °C). The two processes are compared in Table 2. Their total leaching efficiency is similar for Pb (90–92%), whereas Ni (66%) and Zn (70%) leaching is higher for pressure leaching. On the contrary, Cu leaching is higher (85%) in the two-step process. In the 2nd leaching step of two-step leaching process Cu, Ni, and Zn could be more concentrated by 2–3 times compared to the pressure leaching process due to a lower L/S ratio. The composition of the residues after metal removal was also compared. In the residue of the two-step leaching process, which includes roasting, Fe contents were above 60% which meets the criteria for direct use as secondary iron ore with a very low S content (1%). In the residue after pressure leaching, Fe and total S content were 52% and 16%, respectively. Compared to the initial material (Table 1), Fe content is slightly higher (increase from 50 to 52 wt%) due to precipitation of the Fe(NO₃)₃ reagent, while around 20% of sulfur goes into solution (decrease from 20 to 16 wt%). After roasting, the composition of the residue from the pressure leaching is similar to that of the residue from the two-step leaching test. Fig. 11 shows the XRD patterns of the pressure leaching residue before and after roasting. It confirms that the residue after roasting consists of Fe₂O₃ as a dominant phase with trace amounts of PbSO₄ (anglesite), and can thus also be used as an iron ore.

Based on the results shown above, two processes were suggested to selectively leach Pb, Cu, Ni and Zn from matte and simultaneously transform the FeS matrix in an Fe-oxide rich material (Fig. 12). Both processes require a roasting step to oxidize the FeS matrix material in view of total recycling. Meanwhile, the two-step leaching process is superior since a more concentrated solution of Cu, Ni, and Zn (2–3 times higher compared to the pressure leaching process due to difference in L/S ratio) is produced in the 2nd leaching step. Additionally, the 2 stage leaching process requires a lower capital cost for leaching (atmospheric condition, smaller reactor) even if it is a more complex leaching process (2-step). Also, the leachate of the 1st leaching step can be reused as leaching agent of in the same 1st step after Pb removal through PbSO₄ precipitation until a certain amount of Cu, Ni, and Zn has been accumulated in the solution. Then it can be sent to the separation and purification process to recover Cu, Ni, and Zn.

3.4. Metal recovery from leachate

For both the two-step leachate (Fe(III)-HNO₃ leaching and water leaching after roasting, L1) as well as for the leachate from the one-step pressure leaching (L2), the recovery of Cu, Zn and Ni was studied. Both samples were considered interesting for further processing, with the two-step leachate having a considerably higher concentration of Cu (1477 mg/L) and the one-step leachate resulting from a more efficient leaching for Zn (70%) and Ni (66%). Separation of Cu, Zn and Ni was investigated by the principle of ion-exchange adsorption with DTPA-functionalized chitosan-silica. The structure of this adsorbent material is shown in Fig. 13. Prior to recovery by adsorption, lead was removed from the two-step leachate (L1). The Pb concentration after the first step (Fe(III)-HNO₃) was high enough to allow easy recovery by precipitation as PbSO₄. In the one-step leachate (L2) Pb was not removed, in order to investigate the possibility of separating lead by ion exchange, together with the other metals. The resulting compositions of the leachates used in the recovery study are presented in Table 3.

3.4.1. Precipitation of Fe(III) in a pre-hydrolysis step

Selectivity arises from the immobilization of the organic ligand DTPA. DTPA shows a different affinity for different metal ions, based on the stability constant of the complex that is formed between the organic ligand and the chelated metal ion. By comparison of literature values of stability constants between free DTPA and certain metal ions, one can have a good estimation about the relative affinity of the corresponding metal ions for DTPA-immobilized chitosan-silica particles. Some relevant stability constants reported in the literature are summarized in Table 4.

From Table 4, it appears that DTPA has the highest affinity for Fe (III), compared to the other metal ions shown here. As a consequence, the presence of Fe(III) ions in a leachate sample will hamper the complexation of the other metal ions present in solution. This competition effect was confirmed by performing an adsorption experiment from a synthetic mixture of Fe(III), Cu(II), Ni(II) and Zn(II). It was observed that the adsorption of Fe(III) caused saturation of the adsorbent and thus no Cu(II), Ni(II) or Zn(II) ions were removed from solution. To eliminate the competition with Fe(III), it should either be reduced to Fe (II) or removed from the solution. By reduction to Fe(II), the stability constant, and thus affinity, significantly decreases, resulting in a lower amount of iron adsorbed in favor of the other metal ions. However, complete removal of iron from solution was considered a better option, in order to fully prevent any iron from contaminating the available
Removing Fe(III) from solution is very easy by hydrolysis. By increasing the pH to 3–4, Fe(OH)₃ precipitates and can be easily separated from solution by centrifugation, without affecting the concentration of the other ions present in the leachate, since these start to hydrolyze at higher pH values. Note that also Fe(II) starts to hydrolyze at higher pH values. In order to make sure that all iron in solution was at the +III oxidation state, some droplets of hydrogen peroxide solution were added to the leachate (Morgan and Lahav, 2007). The new composition of leachate L1 is shown in Table 5.

### 3.4.2. Metal recovery from leachate L1

After precipitating Fe from the leachate, adsorption from this leachate was investigated. From Fig. 14, it can be observed that the sorbent is able to recover Cu and Ni nearly quantitatively from solution. Ca is not adsorbed, which is in agreement with our aims, as adsorption

---

**Table 2**

<table>
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<tr>
<th>Elements</th>
<th>1st leaching (%)</th>
<th>Total leaching (%)</th>
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<td>0.4</td>
</tr>
<tr>
<td>Cu</td>
<td>22</td>
<td>85</td>
<td>0.2</td>
<td>60</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Ni</td>
<td>31</td>
<td>41</td>
<td>0.1</td>
<td>66</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>22</td>
<td>61</td>
<td>0.1</td>
<td>70</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>ND*</td>
<td>ND*</td>
<td>1</td>
<td>ND*</td>
<td>15.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Mass loss (%)</td>
<td></td>
<td></td>
<td>40</td>
<td></td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

* ND: not determined.

b After roasting of the residue from pressure leaching (roasting temperature: 600 °C for 2 h).
of Ca, present in a comparable concentration with Ni, would contaminate the resin with unwanted ions. Pb and Zn are partially removed from solution. At pH = 2.03, a recovery of 84.13% and 77.92% was obtained for Pb and Zn, respectively. This is due to their lower (and comparable) affinity for DTPA. Note also for Pb and Zn that adsorption increases as a function of pH. This has to do with the deprotonation of carboxylic acid functional groups of DTPA by increasing the pH. An increase of the negative charge density on the ligand, immobilized on the chitosan-silica matrix, is in favor of ionic interactions with the positively charged, free metal ions in solution.

The selective ion exchange observed in the batch adsorption experiments was exploited in a column-chromatography setup. A column consists of a solid phase of functionalized material through which a solution flows. This not only allows to recover metals from the leachate, but also to separate them from each other. By collecting all single-element fractions, pure metal solutions can be obtained. Possible measures that could improve the separation of nickel and copper, so that for these ions too, pure metal fractions could be obtained. Possible measures that could be taken to achieve a better separation are the use of a longer column, a lower flow rate, a slower decrease in pH, etc. The latter was applied in the next experiment.

4.3.3. Metal recovery from leachate L2

Also for leachate L2, the metal recovery was investigated by the principle of column chromatography. The resulting chromatogram is presented in Fig. 16. Compared to the previous separation experiment (Fig. 15), a slower decreasing pH gradient was applied here. As a result, breakthrough of the different metal ions occurred more carefully. The metals Cu, Zn and Ni were separated well from each other. The possibility of also recovering Pb by ion exchange was investigated. Unfortunately, it eluted together with Ni. Since the corresponding

![Fig. 15. Column separation experiment with leachate L1. The cumulative breakthrough is reported as a function of elution volume. A decreasing pH gradient (increasing \([\text{HNO}_3]\)) was applied.](image-url)
affinity values are too close to each other, it seems to be a better option to remove lead first by precipitation with sulfate, as described above. In that case, pure solutions of both Zn, Ni and Cu can be obtained from the leachate originating from the matte.

The performance of the DTPA-functionalized chitosan-silica material as the stationary phase in a lab-scale chromatography column is promising. The porosity was found to be sufficient to ensure a fluent flow (liquid percolation) through the column. Also the ease with which the column could be desorbed and reused in repetitive separation experiments was high, thus revealing a high potential use outside of the laboratory as well. Nevertheless, it is clear that the tested elution setup results in an average 10-fold dilution of the metal concentration in the column fractions compared to the initial leachate. It may be considered to concentrate the leachate feed prior to column separation or to concentrate the column fractions by evaporation. In both cases, an economically feasible implementation of this technique for the recovery of base metals will require further optimization of the elution parameters, to increase the metal concentration in the respective column fractions. During industrial process development, continuous, sequential column configurations could further improve the final concentrations. Nonetheless, it was shown that separated fractions of Cu, Ni and Zn could be collected from a leachate of a lead-smelter residue by one simple column-chromatography cycle. In the presence of the strongly basic sulfide anion, Cu, Zn and Ni form highly insoluble metal salts, even at low pH. Hence, by addition of hydrogen sulfide these metal ions could be precipitated from the diluted column fractions.

4. Conclusions

Two possible routes, two-step nitric acid leaching and one-step oxidative pressure leaching, were investigated to selectively recover Pb and other minor metals (Cu, Ni, Zn) from lead smelter residue, matte. The two-step leaching process consists of Fe(III)-HNO₃ leaching in the first step and roasting, followed by water leaching in the second step. In the first step, Pb leaching was 90% at the optimum condition: L/S ratio 8, 0.5 mol L⁻¹ HNO₃, 0.15 mol L⁻¹ Fe(III), 25 °C. In the second step, roasting at 600 °C followed by water leaching at 50 °C selectively leached Ni, Cu, and Zn with a complete conversion of Fe sulfides to oxides. In the final residues, Fe content was above 60% which can be directly used as secondary iron ores in blast furnaces. With the one-step pressurized leaching in nitric acid, Pb, Cu, Ni, and Zn could be leached simultaneously without dissolving the matrix materials. At the optimal condition (130 °C, 60 min, 0.3 mol L⁻¹ HNO₃, 0.07 mol L⁻¹ Fe(III), L/S ratio 20), Pb, Cu, Zn and Ni leaching were 92, 60, 70 and 66%, respectively, while Fe leaching was limited to 2%. The pressure leaching would be more economical and environmentally friendly (i.e. lower SOₓ emission and operating temperature, and simple process). In a next stage, it was possible to fully recover the valuable metals Cu, Zn and Ni from the leachates by ion-exchange adsorption. DTPA-functionalized chitosan-silica was used as the stationary phase in column chromatography to mutually separate Cu, Ni and Zn from each other. Separated fractions were obtained by applying a decreasing pH gradient. Pb and Fe were removed from the leachates in a pre-treatment step: Pb by sulfate precipitation and Fe by hydrolysis. The investigated leaching and metal recovery methods can be combined as process steps of two possible routes for the selective recovery of Pb (90–92%), Cu (85–60%), Ni (41–66%), and Zn (61–70%) from the studied secondary lead smelting residue. Comparing the two investigated processes, the two-step leaching seems to be superior for getting concentrated solutions of Cu, Ni, and Zn in the 2nd leaching step (2–3 times higher) and it requires a lower capital cost for leaching (due to atmospheric leaching condition and smaller reactor sizes) even if it is a more complex leaching process (2-step).

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